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(54) POLYMERISATION PROCESS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the polymerisation of propylene.

British Patent 853,127 claims the polymerisation of propylene using a catalyst which is generally of the Ziegler type, preferably in the presence of an inert hydrocarbon solvent, by polymerising propylene at a temperature in excess of its critical temperature, preferably 100—250°C, and preferably under a minimum pressure of propylene which is directly proportional to the temperature, being at least 1000 p.s.i. at 100°C and 11,000 p.s.i. at 250°C.

In the specification of British Patent 853,127, it is stated that the polymerisation is preferably carried out in the presence of a diluent containing the active catalyst in either dissolved or finely dispersed form.

A variety of catalysts are used in the Examples, the metal components being VCl_4 , $TiCl_4 + VCl_4$, $TiCl_4$ and $TiCl_4 + VOCl_3$; the activator being aluminium tri-isobutyl or lithium aluminium tetraheptyl. The polypropylene obtained is stated to be a crystalline material.

According to the present invention there is provided a process of polymerising propylene wherein propylene is polymerised at a temperature in excess of 100°C and a pressure of at least 600 atmospheres using a Ziegler type catalyst which is a combination of an organo-aluminium activator and solid compound of a transition metal of sub-groups IVA to VIA of the Periodic Table, wherein said solid compound of a transition metal has been finely dispersed by using the said solid compound, either alone, or in the presence of the organo-

aluminium activator, as a catalyst for the polymerisation of a minor proportion of up to 100 moles/mole of transition metal compound of an α -olefine under conditions to produce an amorphous polymer (as hereinafter defined).

Since the process is operated at a temperature of propylene, it will be appreciated that the propylene will be gaseous under all conditions of pressure.

The polymer obtained by the process of the present invention is polypropylene of low crystallinity. By adjusting the reaction conditions the molecular weight of the polymer can be varied within quite wide limits. Thus, using a low polymerisation temperature, such as 110°C and a high pressure such as 2500 atmospheres, the polymer obtained has a relatively high molecular weight as indicated by a melt flow index (measured by ASTM Test Method 1238—62T using a 2.16 kgm weight at 190°C) of 2.4. However, using a polymerisation temperature of 170°C or higher a low molecular weight product (MFI is 1000 or more) is obtained. Using intermediate reaction conditions, polymers of differing characteristics can be obtained.

It is preferred to operate a single phase system, and to obtain a single phase, a pressure of at least 600 atmospheres is used. Higher pressure are preferred, a convenient pressure being about 2000 atmospheres, although pressures up to about 3000 atmospheres or possibly even above this, can be used if this is desired.

It should be appreciated that the present invention offers several advantages over the low pressure processes using Ziegler catalysts. Thus, the low pressure process in many cases is effected using a suspension of catalyst in an inert hydrocarbon diluent in which the olefine monomer is dissolved. This process is slow, taking several hours, and uses substantial quantities of catalyst relative to the amount of polymer produced. Furthermore, in effecting polymerisation in diluent, some soluble

polymer can be formed and this can result in a viscous slurry being obtained which is difficult to handle. With the process of the present invention, conversion is attained quickly, typically in less than four minutes. In general the conversion of monomer to polymer relative to the amount of catalyst used is greater using the present process than is attained using conventional low pressure processes using Ziegler catalysts in a diluent. Finally it is preferred that the process is carried out at high pressure in a single fluid phase under conditions such that the polymer produced does not form a separate solid or liquid phase. Solutions of polymers in a supercritical gas have a low viscosity, which is much less than that of the liquid phase when effecting polymerisation in a liquid diluent at low pressure, and thus it is desirable and advantageous to operate, in as far as this is possible, with monomer mixtures in the supercritical state.

The transition metals, the compounds of which may be used in the process of the present invention, include zirconium, vanadium and particularly titanium. Suitable compounds of vanadium can be prepared by the reduction of a solution of hydrocarbon soluble vanadium compound with an organo-aluminium reducing agent, to give a precipitate of an insoluble vanadium compound wherein the vanadium has a decreased valency. Suitable vanadium compounds for this purpose include VOCl_3 and VCl_4 which can be reduced using compounds such as aluminium triethyl or aluminium diethyl halide.

However, we prefer to use titanium compounds and in particular titanium trichloride. The term "titanium trichloride" is used in the manner common in the art to include not only pure titanium trichloride, but also compositions in which titanium trichloride is associated with other materials particularly with aluminium compounds such as aluminium trichloride. The various forms of titanium trichloride which can be used may be prepared as follows:

(1) Pure titanium trichloride may be obtained as the product obtained by heating a mixture of TiCl_4 vapour and hydrogen, or by heating together the stoichiometric quantities of TiCl_4 and titanium metal.

(2) A product sold commercially and referred to as titanium trichloride is made by the reduction of TiCl_4 with metallic aluminium has the approximate empirical formula $\text{AlTi}_3\text{Cl}_{12}$ and is a mixed crystal of TiCl_3 and AlCl_3 in the approximate molar proportions of 3:1. This material may be prepared by adding metallic aluminium and aluminium trichloride to TiCl_4 being heated under reflux and then separating the mixed crystal product from the excess unreacted TiCl_4 , for example by distillation at low pressure as described in British Patent No. 877,050. Preferably the product is ground before being used as a catalyst, for

example in a dry ball-mill. Alternatively, the mixed crystal product may be obtained by ball-milling an excess of titanium tetrachloride, with metallic aluminium for example at temperatures up to 200°C .

(3) A particularly preferred method of preparing titanium trichloride is by reacting titanium tetrachloride with aluminium alkyls or aluminium halogen alkyls, for example aluminiumtriisobutyl, aluminiumdiisobutyl monohydride, aluminiummonoethyldichloride, aluminiumdiethyl monofluoride, and preferably aluminiumdiethyl monochloride or aluminiumethyl sesquichloride. The titanium tetrachloride and the organo-aluminium compound are reacted at a temperature in the range from -100°C to $+100^\circ\text{C}$, and advantageously from -20°C to $+40^\circ\text{C}$, the molar ratio of aluminium to titanium being 0.1 to 4.0 and preferably 0.3 to 2.0. The brownish red trivalent titanium precipitate thus obtained can be heated at once for 1 to 5 hours at 60 to 120°C , or the precipitate can be washed with an inert organic medium such as that in which the reduction of the tetravalent titanium to the trivalent titanium has taken place, and then heated. The precipitated titanium trichloride component may be heated more than once if this is desired. Care must be taken that all the operations are carried out with the exclusion of oxygen and moisture. The titanium trichloride component thus obtained contains aluminium chloride and will normally also include an organo-aluminium halide.

If desired mixtures of the transition metal compounds can be used, for example a mixture of titanium and vanadium chloride.

In describing the technique of dispersing the catalysts, the term "amorphous polymer" is used to include polymers which, under the particular polymerisation conditions used, are swollen by the diluent and cause fracturing of the catalyst particles. These "amorphous polymers" may be the polymers of monomers which under normal polymerisation conditions form crystalline polymers and do not cause breakdown of the catalyst particles.

The production of the solid transition metal compound as a fine dispersion by using the said compound, either alone or together with the organo-aluminium activator as a catalyst for the production of a minor proportion of an amorphous polymer can be referred to as the "catalyst pretreatment" or simply "pretreatment" and a large number of different catalyst pretreatments may be used. The preferred solid transition metal compound is titanium trichloride and the pretreatment steps enumerated below are described in respect of the use of titanium trichloride.

(A) To titanium trichloride there is added an organo-aluminium activator such as an aluminium alkyl or preferably an aluminium halogenalkyl. The polymerisation catalyst thus produced is then used to polymerise an un-

branched α -olefin containing at least 5 carbon atoms, advantageously pentene-(1), hexene-(1), heptene-(1), octene-(1) or another such olefine within the range from hexene-(1) to hexadecene-(1), the polymerisation being effected either in the undiluted α -olefines themselves or in their solutions in an oxygen-sulphur- and olefine-free organic media, for example an aromatic, aliphatic or cycloaliphatic hydrocarbon. It is advantageous to choose the proportion of trivalent titanium to α -olefine contained in the polymerisation catalyst in a manner such that for each trivalent titanium atom, 3 to 20, preferably 5 to 20, α -olefine molecules are present. Preferably the polymerisation of the specified unbranched α -olefines is effected at temperatures of 60°C and below, for example 50°C and even room temperature. The catalyst thus obtained is dispersed in a finely divided, virtually colloidal, form and substantially all the particles have a diameter not exceeding 5 microns and in many cases less than 1 micron.

(B) As in pretreatment procedure (A), an organo-aluminium activator is added to the titanium trichloride. This catalyst system is then used to polymerise an α -olefine selected from ethylene, propylene and butene-1 at a temperature of at least 60°C. For ethylene and propylene a temperature of at least 100°C should be used, whilst for butene-1 the desired dispersion effect may be obtained at a temperature of about 60°C and above, the temperature used for the pretreatment being dependent primarily on the α -olefine being polymerised. The amount of α -olefin used should be sufficient to fracture the catalyst and a convenient amount is 8–10 moles of an α -olefine per mole of trivalent titanium. Preferably this pretreatment is effected in an inert diluent.

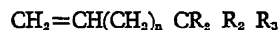
(C) This is similar to pretreatment (B) in that it involves the pretreatment of the titanium trichloride and organo-aluminium activator with an α -olefin at elevated temperature. In this case the α -olefines are the branched chain α -olefines such, for example, 3-methyl butene-1, 3-methyl pentene-1, 4-methyl pentene-1. The polymerisation conditions used are such that these α -olefines are polymerised to give an amorphous polymer. The polymerisation temperature used should be at least 100°C.

(D) This is similar to pretreatment (A) in that the pretreatment involves the use of both the titanium trichloride and the organo-aluminium activator. In this pretreatment a mixture of α -olefines is copolymerised to give an amorphous copolymer in which the monomer constituents are randomly distributed within the polymer chain. The temperature of the pretreatment may conveniently be in the range 20° to 100°C and in general a temperature of about 60°C will be satisfactory. Suitable monomer mixtures for the pretreatment in-

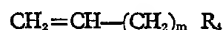
clude, for example, ethylene/propylene, ethylene/butene-1 and propylene/butene-1. Mixtures of the linear α -olefines of pretreatment (A) can also be used. The quantity of monomers used in this pretreatment may be up to 100 moles per mole of trivalent titanium.

(E) In this pretreatment the titanium trichloride is used as a polymerisation catalyst in the substantial absence of added organo-aluminium activator. The absence of added organo-aluminium activator does not preclude the presence of small amounts of activator which may be present in the titanium component as a result of its method of preparation. The α -olefine used in the pretreatment is at least one α -olefine of from 2 to 16 carbon atoms including for example, ethylene, butene-1, 4-methyl pentene-1, octene-1, decene-1, dodecene-1, tetradecene-1, and hexadecene-1. The treatment is conveniently effected at a temperature in the range 0–50°C and the amount of α -olefine used is in the proportion of 0.2 to 2.5 moles of monomer per mole of trivalent titanium. The actual amount of monomer is dependent on the nature of the monomer, but in general 1.5 moles of monomer per mole of titanium provides a satisfactory effect.

(F) The titanium trichloride, together with an organo-aluminium compound, is used to polymerise a minor proportion of an α -olefine in the presence of a polymerisation inert diluent which is a saturated or unsaturated cyclic compound the α -olefine being a branched chain olefine of formula:—



or an olefine of formula



where

n is 1 or 2

m is 0, 1 or 2

R₁ is hydrogen or an alkyl group

R₂ and R₃ are alkyl groups and

R₄ is a cycloalkyl, cycloalkenyl or aromatic ring system which ring system may be substituted with alkyl groups. The inert diluent can be cyclohexane, methylcyclohexane, cyclohexane, benzene, toluene, chlorobenzene, tetralin and decalin. The monomers can be 4-methyl pentene-1, 5-methyl hexene-1, vinyl cyclohexane or styrene. Mixtures of the specified monomers may be used or a mixture of one such olefine with a minor proportion of a further α -olefine monomer particularly the higher unbranched α -olefines such as hexene-1, octene-1, and decene-1. The dispersion is effected at a temperature in the range 30 to 80°C and the effectiveness of the treatment is dependent on the combination of diluent and monomer used. With 4-methyl pentene-1, effective dispersion is obtained with cyclohexane or cyclohexene whilst with styrene

good dispersion is obtained in benzene. This technique of obtaining a dispersed catalyst is described and claimed in British Patent No. 1,295,681.

5 The amount of monomer used in the pre-treatment will vary in dependence on the monomer, catalyst and temperature being used and up to 100 moles of monomer can be used if desired but in general up to 20 moles of
10 monomer (or mixture of monomers) is sufficient to provide a finely dispersed catalyst.

The formation of the catalyst as a fine dispersion makes it particularly suitable for continuous operation and continuous injection
15 into the reactor since the fine particles can be pumped using a high pressure pump which would be damaged by the use of coarse particles.

Chain transfer agents such as hydrogen
20 may, if desired, be used in the reaction to lower the molecular weight and hence raise the melt flow index of the product. However, the molecular weight of the polymer product is dependent not only on the presence or absence of a chain transfer agent, but also on the reaction
25 conditions, including the temperature, and in general the use of chain transfer agent is not necessary in the present polymerisation process since sufficient control of the molecular weight is obtained by varying the reaction conditions.

30 The polymerisation process can be carried out as a batch operation but it is preferred to effect the polymerisation on a continuous basis. When operating on a continuous basis, the process may be carried out in a continuous stirred reactor or a continuous tubular reactor. The process may be carried out as a single zone process using a single reactor, or in a
35 multi-zone process using either a number of reactors in series, optionally linked by coolers or a single reactor which is effectively divided internally into several zones, that is two or more zones. Under the reaction conditions usually employed, the catalyst is active for
40 only a short time of the order of several seconds, for example 10 seconds, and thus in a multi-zone process it will normally be necessary to introduce the catalyst into more than one zone. The half-life of the catalyst utilised
45 will depend on the reaction conditions, particularly temperature, and with longer catalyst life times, longer residence times of the monomers in the reactor will be required. The polymer formed in the reactor reactors may be separated from the unreacted monomers and processed in the normal high pressure fashion. The conversion of monomer to polymer based
50 on the amount of catalyst used will be greater than in the more conventional Ziegler process using diluents at low pressure and in some cases the conversion may be sufficiently high for the removal of catalyst residues to be unnecessary. The unreacted propylene is mixed with a further quantity of propylene, represented and recycled to the reactor.
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The catalyst is introduced by injecting it as a fine dispersion in a suitable inert liquid directly into the reactor. Suitable liquids include, for example, white spirit, hydrocarbon
70 oils, pentane, hexane, heptane, toluene, higher branched saturated aliphatic hydrocarbons and mixtures of such liquids, for example a mixture of branched saturated aliphatic hydrocarbons having a boiling point range 168 to 187°C. The dispersion is kept out of contact with
75 water and air, preferably under a nitrogen blanket, before it is introduced into the reactor and the propylene also should be essentially free of water and oxygen.

The propylene homopolymers produced in accordance with the present invention have properties similar to those of some ethylene/vinyl acetate copolymers, but do not contain the polar monomer which gives such copolymers low thermal stability. The propylene
80 polymers of the present invention are thus suitable for use in some of those applications which have been proposed for ethylene/vinyl acetate copolymers. In some applications the new propylene homopolymers may be more
85 suitable than the ethylene/vinyl acetate copolymers which have a higher electrical power factor than the hydrocarbon polymers.

The following examples are illustrative of the present invention.
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EXAMPLES 1-3.

A catalyst based on titanium trichloride was used. The titanium trichloride catalyst component was prepared by reaction of TiCl_3 and aluminium ethyl sesquichloride in a purified
100 hydrocarbon fraction comprising a mixture of branched saturated aliphatic hydrocarbons having a boiling point range 170-190°C. A solution of the sesquichloride in this diluent was added gradually drop by drop, with stirring, to a solution of TiCl_3 in the same diluent
105 over a period of several hours, the temperature being held at 0°C. The molar ratio of total aluminium to titanium was approximately 1.6. The resulting slurry containing TiCl_3 was subsequently heated for a period at 95°C. The
110 TiCl_3 was then washed several times with fresh quantities of the diluent. To a slurry of the titanium trichloride precipitate was added aluminium diethyl chloride in a molar proportion of aluminium to titanium of 4:1. This system was then used to polymerise 4 moles of decene-1 per mole of titanium at 40°C to give a finely dispersed catalyst which was used
115 for the polymerisation of propylene.

Propylene was introduced into a continuous stirred autoclave reactor under conditions of temperature and pressure as indicated in the table. The slurry of decene-1 treated catalyst was diluted to a concentration of about 0.01 M
120 based on titanium by the addition of cyclohexene and the diluted catalyst slurry was then introduced into the reactor.

The melt flow index (M.F.I.) of the polymer
125

was measured using the method of ASTM Method 1238—62T using a 2.16 Kgm weight at 190°C.

The experimental details and the results obtained are set out in the table below.

Example	Pressure (K-gm/cm ²)	Temperature (°C)	Monomer feed rate (Kgm hr ⁻¹ litre ⁻¹)	Efficiency Mol polymerised Mol Ti in catalyst	M.F.I.	Crystallinity (%)	Tensile Yields Stress (MN/m ²)	Break Stress (MN/m ²)	Elongation (%)
1	2500	110	11	10,000	2.4	24	3.1	11.3	1250
2	2000	170	11	17,000	4000	N.D.	N.D.	N.D.	N.D.
3	2500	130	11	10,000	13	21	N.D.	N.D.	N.D.

N.D. indicates not determined.

The % crystallinity was determined by X rays. The mechanical properties were measured on unannealed compression moulded specimens.

It will be appreciated that many variations of the present invention, as illustrated by the examples are possible.

WHAT WE CLAIM IS:—

1. A process of polymerising propylene wherein propylene is polymerised at a temperature in excess of 100°C and a pressure of at least 600 atmospheres using a Ziegler type catalyst which is a combination of an organo-aluminium activator and solid compound of a transition metal of sub-groups IVA to VIA of the Periodic Table, wherein said solid compound of a transition metal has been finely dispersed by using the said solid compound, either alone, or in the presence of the organo-aluminium activator, as a catalyst for the polymerisation of a minor proportion of up to 100 moles/mole of transition metal com-

pound of an α -olefine under conditions to produce an amorphous polymer (as hereinbefore defined).

2. A process according to claim 1 wherein the pressure is 2000 atmospheres or above.

3. A process according to claim 1 or 2 wherein the transition metal compound is a compound of zirconium, vanadium or titanium.

4. A process according to claim 3 wherein the transition metal compound is titanium trichloride.

5. A process according to claim 4 wherein the titanium trichloride is the product of reacting titanium tetrachloride with an aluminium alkyl or an aluminium alkyl halide.

6. A process according to any of claims 1 to 5 wherein the transition metal compound has been dispersed by using it together with an organo-aluminium activator, as a catalyst for the polymerisation of an unbranched α -olefine containing at least 5 carbon atoms.

7. A process according to any of claims 1 to 6 wherein in the production of the amorphous polymer up to 20 moles of monomer or monomers are polymerised per mole of transition metal in the transition metal compound.
8. A process according to any of the preceding claims whenever carried out on a continuous basis in more than one zone.
9. A process for polymerising propylene substantially as hereinbefore described with reference to the examples.
10. A propylene polymer whenever prepared by the method of any of the preceding claims.

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